DOT/FAA/AR-01/117

Office of Aviation Research
Washington, D.C. 20591

A Microscale Combustion Calorimeter

February 2002

Final Report

This document is available to the U.S. public
through the National Technical Information
Service (NTIS), Springfield, Virginia 22161.

U.S. Department of Transportation
Federal Aviation Administration

20020517 103

NOTICE

1. Report No. DOT/FAA/AR-01/117	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle A MICROSCALE COMBUSTION CALORIMETER		5. Report Date February 2002
		6. Performing Organization Code
7. Author(s) Richard E. Lyon and Richard Walters*		8. Performing Organization Report No.
9. Performing Organization Name and Address Federal Aviation Administration William J. Hughes Technical Center Airport and Aircraft Safety *Galaxy Scientific Corp. Research and Development Division 2500 English Creek Ave., Bldg. C Fire Safety Section Egg Harbor Township, NJ 08234 Atlantic City International Airport, NJ 08405		10. Work Unit No. (TRAIS)
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Aviation Research Washington, DC 20591		13. Type of Report and Period Covered Final Report
		14. Sponsoring Agency Code AIR-120

15. Supplementary Notes

The FAA William J. Hughes Technical Center COTR is Richard Lyon

16. Abstract

A method for measuring the heat release rate of milligram-sized samples is described in this report. Pyrolysis-combustion flow calorimetry (PCFC) separately reproduces the solid-state and gas phase processes of flaming combustion in a nonflaming test by rapid controlled pyrolysis of the sample in an inert gas stream followed by high-temperature oxidation (combustion) of the pyrolyzate in excess oxygen. The rate at which the sample releases its heat of combustion is calculated from the oxygen consumption history. The heat of combustion is obtained from the time integral of the heat release rate.

17. Key Words Polymer, Fire, Flammability, Thermal analysis, Combustion, Calorimetry; Fire hazard; Heat release rate; Oxygen consumption	18. Distribution Statement This document is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 28	22. Price

Form DOT F1700.7 (8-72)   Reproduction of completed page authorized

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

A method for measuring the heat release rate of milligram-sized samples is described in this report. Pyrolysis-combustion flow calorimetry (PCFC) separately reproduces the solid-state and gas phase processes of flaming combustion in a nonflaming test by rapid controlled pyrolysis of the sample in an inert gas stream followed by high-temperature oxidation (combustion) of the pyrolyzate in excess oxygen. The rate at which the sample releases its heat of combustion is calculated from the oxygen consumption history. The heat of combustion is obtained from the time integral of the heat release rate.

BACKGROUND

The rate at which heat is released by a burning material is the single most important parameter determining its hazard in a fire, particularly in an enclosed space such as a building, a ship, or an aircraft cabin [1, 2, and 3]. Several different bench scale methods have been developed for measuring heat release rate during flaming combustion of materials, products, and components [4 and 5]. These bench scale fire calorimetry methods require replicate samples on the order of a 100 grams each, and the results are highly dependent on the ignition source [6], sample thickness [7], sample orientation [8], ventilation [9], and edge conditions [8], all of which combine to make the test data configuration dependent and to obscure the effect of material properties and composition on burning behavior.

The desire for a quantitative analytical laboratory test that correlates fire behavior or flame test performance with material properties has been the motivation to relate thermogravimetric analyses to flammability [10, 11, 12, and 13]. To date, most thermogravimetric investigations of flammability have relied on a single thermal stability parameter (e.g., char yield or thermal decomposition temperature) to relate the chemical composition of a material to its fire or flame test performance (e.g., char yield versus limiting oxygen index). Individually, these thermal stability parameters have found limited success as material descriptors of flammability and their interrelationship in the context of flaming combustion has remained obscure until recently, when it was shown that a particular combination of thermal stability and combustion parameters could correlate fire behavior [14].

Laboratory methods that directly measure heat release rate of milligram-sized samples of materials have been developed to study the effect of material properties and chemical composition of materials on combustibility under controlled conditions. Susott [15, 16, and 17] was the first to measure the heat of combustion of organic materials using transient heating and oxygen consumption. In Susott's method, milligram-sized samples of forest products (foliage, wood, stems, and bark) were pyrolyzed in an inert gas stream at a constant rate of temperature rise, and the pyrolysis gases were combined with oxygen prior to entering a catalytic reactor. Pyrolysis was conducted under inert gas flow to prevent oxidation of the char residue. The rate of oxygen consumption was determined from the electrolytic oxygen generation rate using a null-balance, closed-loop technique. Only qualitative information was obtained for the dynamics of the fuel generation process because the oxygen consumption signal was distorted by the instrument and, therefore, was not synchronized with the mass loss history of the sample. Pyrolysis residue/char fraction was measured by weighing the sample before and after the test and the heat of combustion of the char was determined separately. Sample heating rates were limited by the dynamic capability of the oxygen generator to less than 16 K/min. The rate of heat released by complete oxidation of the pyrolysis gases during thermal decomposition of the sample was calculated from the measured oxygen consumption rate using an average gross heat of combustion for forest products of 14.0 ± 0.5 kJ/g-O_2. The water produced in flaming combustion is in the gaseous state so the relevant heat of combustion is the net value obtained by subtracting the heat of vaporization of water from the gross heat of combustion. Converting Susott's gross heat of combustion to a net value gives 13.3 ± 0.5 kJ/g-O_2 which is equivalent to the currently accepted value 13.1 ± 0.7 kJ/g-O_2 used in oxygen consumption fire calorimetry [5, 18, 19, and 20] as determined from data on a wide range of organic solids and polymers [21 and 22], as well as liquids and gases [23]. Susott did not measure mass loss during the pyrolysis-combustion experiment but normalized the total heat of combustion of the volatiles to the starting sample mass on an ash-free, dry fuel basis. The gross heat of combustion of the char determined in separate oxygen bomb calorimetry experiments [24] was found to be relatively independent of the fuel type at 32.0 ± 0.9 kJ/g for the 43 typical forest fuels tested.

Parker [25 and 26] claims to have improved on Sussot's nonflaming dynamic combustion method by using a step-change in temperature to pyrolyze the sample at a heating rate considered to be

more typical of the surface conditions in a fire. In Parker's device, samples of cellulose are inserted into a preheated, nitrogen-purged furnace resulting in a rapid uncontrolled temperature change and subsequent pyrolysis. An impinging stream of oxygen is mixed with the inert gas-pyrolyzate stream in a catalytic reactor. Combustion gas concentrations (O_2, CO_2, H_2O) are measured and oxygen consumption is used to calculate the heat release rate of volatile fuel combustion. Although mass loss is not measured directly during the test, transient oxygen depletion and combustion gas generation were used to calculate the mass loss rate of cellulose from its known chemical structure. Babrauskas and Parker [27] later refined Parker's device for the measurement of the fuel/oxygen ratio of fire gases.

Reshetnikov, et al. [28 and 29] used an experimental arrangement similar to Parker [25 and 26] in their study of the gas phase oxidation kinetics of polymer decomposition products. In Reshetnikov's technique, milligram polymer samples are decomposed isothermally in an inert gas stream and excess oxygen is added to the volatile fuel stream at various temperatures to effect oxidation. A gas chromatograph with flame ionization detector was used to sample the fuel stream prior to mixing with oxygen in order to separate and identify the individual products of decomposition. Gas phase oxidation kinetics of the fuel species are computed from the measured oxygen consumption history using isothermal methods of analysis. Reshetnikov's device measures the rate of combustion (oxidation) of the fuel gases but not the rate at which these gases are produced by the decomposing solid as it is heated, the latter being the rate limiting process in a fire.

Lasers have been used to pyrolyze polymers for flammability studies by Price [30] and Angel [31]. The pyrolysis gases were analyzed by mass spectrometry and laser-induced fluorescence of hydroxyl radicals, respectively. In combination with thermochemical calculations of the heat of combustion of the fuel species, laser pyrolysis methods can provide an estimate of the total heat released by the polymer.

Commercial thermogravimetric analyzers (TGA) have been used to thermally decompose milligram samples under controlled heating and environmental conditions for flaming and nonflaming combustion studies. Coupling the TGA to an evolved gas analysis (EGA) detector, which is synchronized with the mass loss signal, provides dynamic (rate) capability during the test and allows for interpretation of the transient evolved gas data in terms of the decomposition kinetics of the solid using established methods of nonisothermal analysis [32, 33, 34, and 35] and thermal degradation models for charring and noncharring polymers [36].

Flaming combustion in a TGA was used by Gracik et al. [37 and 38] in combination with evolved gas (CO, CO_2) analysis to study the flammability of fiber reinforced polymer composites. In Gracik's test, a 50 mg sample is heated at a rate of 20 K/min in air in a commercial thermogravimetric analyzer until ignition occurs. Flaming combustion of the sample in the TGA produces carbon dioxide (CO_2) and some carbon monoxide (CO) which are measured and used to calculate the heat release rate [39]. An advantage of CO_2/CO generation (CDG) calorimetry compared to oxygen consumption calorimetry as a measure of combustion heat is the higher sensitivity and lower cost of the CO_2/CO detector(s), but the method is more sensitive to fuel type. Gracik's method is essentially a scaled down version of the early Factory Mutual Research Corporation fire calorimeter, [40] but uses a controlled heating rate instead of a controlled heat flux to force gasification of the solid.

Nonflaming combustion of volatile fuel products generated in a TGA was used by Kifer [41] who studied fire retarded polymers and wood using a high-temperature flame ionization detector (FID) to burn the pyrolysis gases generated in a nitrogen-purged TGA. The FID signal is proportional to the total carbon in the pyrolysis gases, so that the integrated value, which was assumed to be proportional to the total heat release, was related to the flammability of the material. Walters and

2

Lyon [42 and 43] and Inguilizian [44] determined the heat release rate of milligram samples using controlled heating in a TGA to thermally decompose the polymer and determined the heat release rate of the solid from the product of the maximum mass loss rate in the TGA and the net heat of combustion of the volatile pyrolysis products. Walters and Lyon used oxygen consumption calorimetry to measure the heat of combustion of the pyrolysis products while Inguilizian calculated the heat of combustion from the oxidation thermochemistry of the primary fuel species identified by gas chromatography (GC)-mass spectrometry (MS).

The present method of pyrolysis-combustion flow calorimetry (PCFC) seeks to improve upon laboratory pyrolysis-combustion methods by providing dynamic capability for solids without the need to measure mass loss rate during the test. Because the PCFC combustibility test uses milligram samples rather than the kilogram samples of fire calorimetry, it is microscale by comparison to flaming heat release rate tests.

<center>PRINCIPLE OF OPERATION</center>

Pyrolysis-combustion flow calorimetry measures the rate at which the heat of combustion of the fuel gases is released by a solid during controlled pyrolysis in an inert gas stream. The fuel gases are mixed with excess oxygen and combusted (oxidized) at high temperature, and the instantaneous heat of combustion of the flowing gas stream is measured by oxygen consumption calorimetry. Because gas phase combustion reactions are rapid at flame temperatures of 900°-1200°C the rate at which combustion heat Q is liberated per unit time t in the PCFC or in a fire is limited by the fuel generation rate of the thermally decomposing solid. Thus, the heat release rate dQ/dt is proportional to the mass generation rate of volatile fuel or to the mass loss rate of the solid

$$\dot{Q}_c(t) \equiv \frac{dQ_c(t)}{dt} = h^o_{c,v}(t) \frac{dm_v(t)}{dt} = -h^o_{c,v}(t) \frac{dm_s(t)}{dt} \qquad (1)$$

where the proportionality factor $h^o_{c,v}$ is the enthalpy (heat) of complete combustion of the volatile pyrolysis products of mass m_v, and m_s is the instantaneous residual mass of solid. In a fire, volatiles are generated anaerobically at the surface of the material over a range of temperatures and a distribution of molecular weights and atomic compositions are produced [45], so that in general $h_{c,v}^o$ varies over the mass loss history and cannot be treated as a constant as shown in equation 1. In many cases, low-molecular weight organic and inorganic (e.g., HCl, SO_x) species are cleaved from the polymer backbone and released in the initial stages of fuel generation followed by higher molecular weight organic compounds in the intermediate and latter stages [45 and 46]. For materials which form a carbonaceous char during the fuel generation process, the instantaneous atomic composition of the volatiles will necessarily differ from the atomic composition of the original material [17], with hydrogen being evolved in a secondary, high-temperature decomposition step [13]. Consequently, a constant heat of combustion for the volatile fuel, which is equal to the heat of combustion of the solid $h_{c,s}^o$, cannot be assumed except for a few cases, e.g., polymers which thermally depolymerize (unzip) exclusively to monomer (e.g., polymethylmethacrylate, polyoxymethylene, poly (α-methylstyrene) or to a single, known species. Thus, $h_{c,v}^o(t)$ must be determined continuously during the course of the fuel generation process to obtain $\dot{Q}_c(t)$ from the mass loss rate. Continuous determination of $h^o_{c,v}$ during fuel generation is time consuming, so average [42 and 43] or instantaneous [44] values of $h^o_{c,v}$ have been used instead.

Thornton [23] made the experimental observation that the net heat of complete combustion of typical organic molecules per mole of oxygen consumed is relatively constant at E = 419 ±19 kJ/mol-O_2 = 13.1 ±0.6 kJ/g-O_2, and is essentially independent of the chemical composition of the combusted material. Sussot [15], Huggett [21], and Babrauskas [22] later confirmed this result for

<center>3</center>

wide range forest products, chemical compounds, and organic polymers, thereby establishing oxygen consumption as the preferred method for determining heat released in flaming combustion. Thus, to a good approximation (±5%), the net heat of complete combustion of the volatile degradation products, regardless of chemical composition is

$$m_v(t) \, h_{c,v}{}^o(t) = E \, \Delta m_{O_2}(t) \tag{2}$$

where $\Delta m_{O_2}(t)$ is the mass of diatomic oxygen consumed. Substituting the time derivative of equation 2 into equation 1

$$\dot{Q}_c(t) = -h^o_{c,v}(t) \frac{dm_s(t)}{dt} = E \, \Delta \dot{m}_{O_2}(t) \tag{3}$$

shows that the instantaneous heat release rate of the solid $\dot{Q}_c(t)$ (Watts) resulting from complete and instantaneous combustion of the volatile decomposition products can be determined from the product of the mass loss rate and heat of combustion of the fuel, or more simply from the mass consumption rate of oxygen $\Delta \dot{m}_{O_2}(t) = \dot{m}^o_{O_2} - \dot{m}_{O_2}(t)$. Equation 3 shows that the rate at which heat is released by combustion of the fuel gases during controlled polymer thermal degradation can be obtained by measuring the mass of oxygen consumed—and this result is independent of the composition of the fuel. The total heat of combustion of the volatiles (Joules) after the pyrolysis process is complete and the rate of oxygen consumption returns to zero is simply the time integral of equation 3

$$Q_c = \int_0^\infty \dot{Q}_c(t) dt = E \int_0^\infty \Delta \dot{m}_{O_2}(t) \, dt \tag{4}$$

While equation 3 provides a means for relating oxygen consumption measured downstream from a pyrolyzer (or burning surface) to the heat release rate history of the polymer, the oxygen signal must be synchronized with the fuel generation (mass loss) history of the sample. Unfortunately, the flow process of combustion gases from the pyrolyzer (or burning surface) to the oxygen analyzer distorts the oxygen signal. While distortion of the oxygen consumption signal does not effect the measurement of the total heat of combustion [15, 25, and 28], the fuel generation history of the solid sample is obscured unless its mass loss rate is measured [37 and 42]. Comparison of PCFC heat release rates to those measured by TGA-GC/MS [44] showed that the oxygen signal of the combustion flow calorimeter could be corrected for instrumental broadening if the dynamic response of the instrument to a known heat release history is measured so that standard techniques of signal deconvolution can be applied. A simple mixing model for the pyrolysis-combustion flow calorimeter (see appendix A), which was confirmed by experiment, gives the heat release rate of the solid in terms of the change in oxygen concentration θ measured at the detector as

$$\dot{Q}_c(t) = E\rho F \left(\theta + \tau \frac{d\theta}{dt} \right) \tag{5}$$

where ρ and F are the gas stream density and volumetric flow rate, respectively, and τ is the response time of the instrument.

Although the laboratory measurement of nonflaming heat release and heat release rate by PCFC is described by equations 4 and 5, respectively, the relationship of these quantities to material

4

properties remains to be demonstrated. It has been shown that the fuel generation process of a combustible material in a fire is anaerobic [47 and 48], so that the methodology of analytical pyrolysis should be applicable to the study of the behavior of materials in fires. In particular, the maximum fractional mass loss rate of a polymer which thermally decomposes completely in a single-step to volatile fuel gases and a residue fraction μ when heated at a constant rate of temperature rise β is [47 and 48]

$$-\frac{1}{m_o}\frac{dm}{dt}\bigg|_{max} = \left(1-\mu\right)\frac{\beta E_a}{eRT_p^2} \tag{6}$$

where E_a is the global activation energy for pyrolysis, T_p is the temperature of maximum mass loss rate, and e, R are the natural number and gas constant, respectively. Multiplying equation 6 by the heat of combustion of the fuel gases gives the maximum specific heat release rate of the solid (W/g)

$$\dot{q}_c^{max} = \frac{\dot{Q}_c^{max}}{m_o} = \left(1-\mu\right)h_{c,v}^o\frac{\beta E_a}{eRT_p^2} = h_{c,s}^o\frac{\beta E_a}{eRT_p^2} \tag{7}$$

where $h_{c,s}^o = (1-\mu)h_{c,v}^o$ is the heat of combustion of the fuel gases per unit initial mass of solid m_o. The maximum specific heat release rate (equation 7) contains only β and material properties which depend on the chemical composition of the material. Normalizing $\dot{q}_c$ for heating rate gives a time- and rate-independent material flammability property η_c, which has the units and significance of a heat [release] capacity [14],

$$\eta_c \equiv \frac{\dot{q}_c^{max}}{\beta} = \left[\frac{\left(1-\mu\right)h_{c,v}^o E_a}{eRT_p^2}\right] = \frac{E\rho F}{\beta m_o}\left(\theta + \tau\frac{d\theta}{dt}\right)\bigg|_{max} \propto \frac{h_{c,s}^o}{h_g} \tag{8}$$

The heat release capacity is proportional to the combustibility ratio [9] in fire science, $h_{c,s}^o/h_g$, where h_g is the total heat required to gasify unit mass of material. The heat release capacity is a true material property in that it depends only on thermodynamic state variables ($h_{c,s}^o$, h_g), is independent of sample size and heating rate, is calculable from polymer structure using additive molar group contributions [14], and can be measured by different methods [44]. The following sections describe the construction, calibration, and operation of a flow calorimeter that measures dynamic (heat release rate) and static (heat release capacity, char yield, and heat of combustion) combustion parameters using only milligram samples and oxygen consumption calorimetry.

INSTRUMENT CONSTRUCTION

Figure 1 is a schematic diagram showing how the component processes of flaming combustion are reproduced in pyrolysis-combustion flow calorimetry. The apparatus is based on Susott's original concept [15, 16, and 17] of linear programmed heating of milligram samples in an inert (nonoxidizing) atmosphere to separate the processes of char formation and gas phase combustion which normally occur in a fire. In the present device, the sample is heated using a linear temperature program, and the volatile thermal degradation products are swept from the pyrolysis chamber by an inert gas and combined with excess oxygen in a tubular furnace at flame temperatures to force complete nonflaming combustion (oxidation) of the fuel. Combustion products CO_2, H_2O, and acid gases are scrubbed from the gas stream and the transient heat release

5

rate is calculated from the measured flow rate and oxygen concentration after correcting for flow dispersion. The maximum (peak) value of the PCFC heat release rate normalized for the initial sample mass and heating rate is a material flammability parameter with units of heat [release] capacity (J/g-K) which depends only on chemical composition of the sample and is proportional to the burning rate of the material in a fire. Time-integration of the PCFC heat release rate gives the heat of complete combustion of the pyrolysis gases and the char yield is measured by weighing the sample before and after the test. If the pyrolysis is conducted in air so that there is no possibility of char remaining after the test, time-integration of the oxygen consumption signal gives the net heat of complete combustion of the solid, as would be determined in a high-pressure oxygen bomb calorimeter [49].

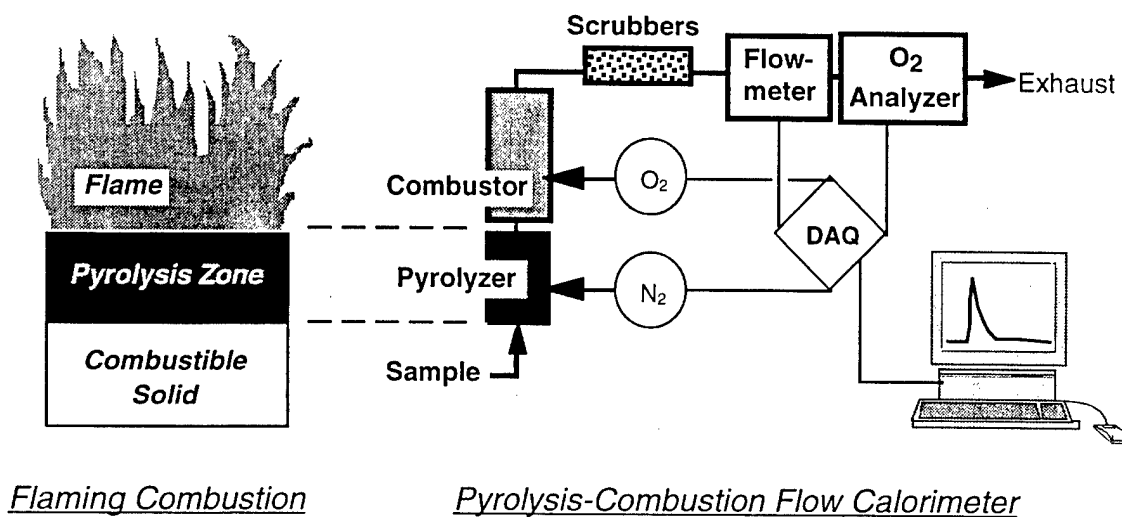Flaming Combustion   Pyrolysis-Combustion Flow Calorimeter

FIGURE 1. SCHEMATIC OF FLAMING COMBUSTION AND
PYROLYSIS-COMBUSTION FLOW CALORIMETRY

PYROLYZER.

Initial studies using a commercial TGA to pyrolyze the polymer samples [42 and 43] were unsuccessful due to condensation of the thermal decomposition products in the TGA cell and heated transfer line. Smearing of the output signal (heat release rate) was also observed because of dilution of the pyrolysis gases with nitrogen in the large mixing volume of the TGA cell. Moreover, the maximum heating rate capability of the TGA (100-200 K/min) was well below the heating rates in fires, which can be as high as several hundred degrees per minute [47]. For these reasons, a temperature-controlled pyrolysis chamber was designed that could be continuously purged with gas, coupled directly to the combustion furnace, and accept a commercial probe pyrolyzer (Pyroprobe 1000/2000, CDS Analytical) to gasify the sample. This arrangement provided consistent temperature and minimum dead-volume with the probe in place for the experiment as shown in figure 2. The probe pyrolyzer body is 6.4 mm in diameter and contains a 3-mm diameter, 25-mm-long platinum resistance coil which heats the sample at a constant rate in the range of $\beta = 20 \times 10^{-3}$ to 20×10^3 K/s. At the highest heating rate, the temperature history of the sample approximates a step change to a preset temperature and in this mode can be used to study the isothermal pyrolysis kinetics of liquids and solids by pulsed heating [50].
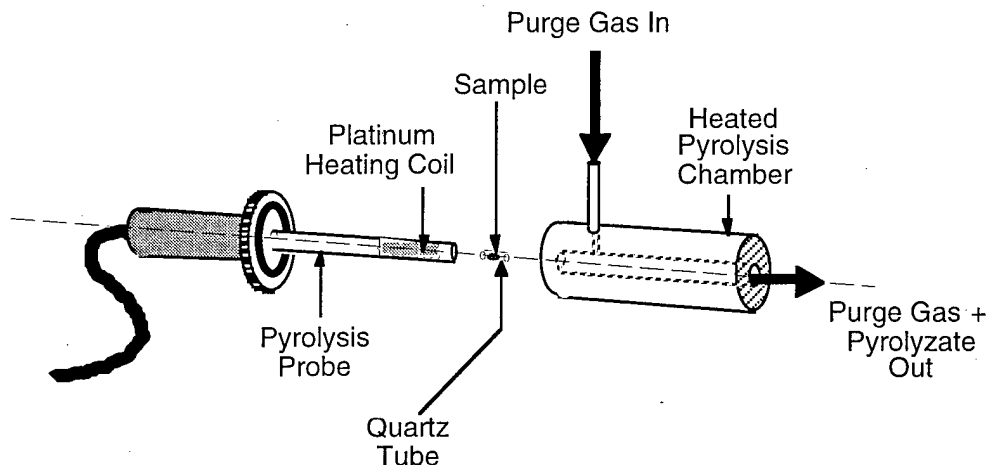
FIGURE 2. PCFC PYROLYZER AND PYROLYSIS CHAMBER

Mass transfer efficiency from the heated pyrolysis chamber to the combustor was studied for a few polymers (polyethylene, polyetheretherketone (PEEK), and KEVLAR™) to determine the minimum temperature necessary to maintain all of the pyrolysis products in the gaseous state entering the combustor. Mass transfer efficiency was calculated as the ratio of the time-integrated heat release rate (total heat of combustion) of the pyrolysis gases at cell temperature T, i.e., $h^0_{c,s}(T)$ to the maximum value obtained in the experiments, i.e., mass transfer efficiency = $h^0_{c,s}(T)/h^0_{c,s}(max)$. The results of these studies are plotted in figure 3 as the mass transfer efficiency versus pyrolysis chamber temperature.   Figure 3 shows that high molecular weight thermal degradation products are generated during pyrolysis which boil at temperatures approaching the decomposition temperature of the polymer.   Loss of these low volatility fuel products by condensation between the pyrolyzer and combustor significantly reduces the peak heat release rate and total heat release unless the pyrolysis chamber temperature is held to within a few degrees of the 1% weight loss temperature of the sample.
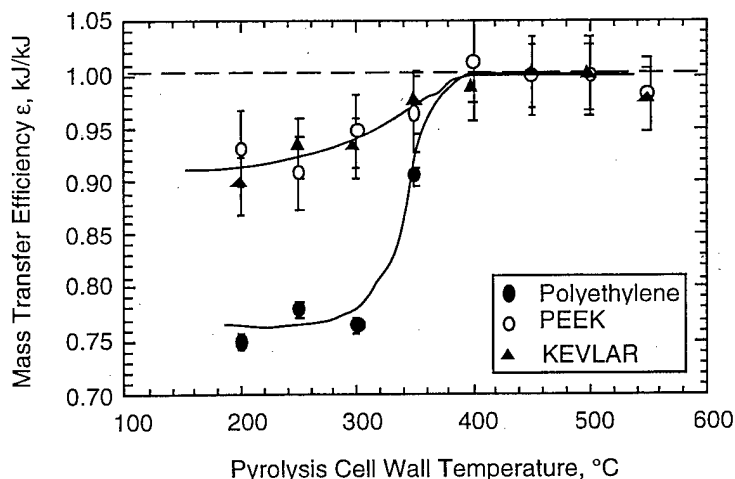

FIGURE 3. EFFECT OF PYROLYSIS CELL WALL TEMPERATURE ON
MASS TRANSFER EFFICIENCY OF PYROLYSIS GASES FOR
PEEK, KEVLAR™, AND POLYETHYLENE

7

A mass flow controller measures and controls the flow of pure (99.99%) nitrogen at 82 cm³/min into the heated pyrolysis chamber to provide an anaerobic pyrolysis environment. Volatile pyrolysis products are swept out of the pyrolysis manifold and 18 cm³/min of pure (99.99%) oxygen is metered into, and mixed with, the nitrogen-pyrolyzate stream prior to entering the combustor. The pyrolysis chamber is held slightly below the decomposition temperature of the sample, as determined in a separate TGA experiment at moderate (10-20 K/min) heating rate, to prevent condensation of high molecular weight decomposition products on the walls of the chamber.

COMBUSTOR.

The combustor is a coiled, 5 meter length of 6.35-mm diameter Inconel tubing having a wall thickness of 0.89 mm, a coiled length of 24 cm, and an outer coil diameter of 5 cm as shown in cross section in figure 4. The coiled combustion tube is contained in a ceramic furnace capable of maintaining a maximum temperature of 1200°C. The Inconel tubing in the ceramic heater is surrounded with 5-cm of ceramic fiber insulation and a 3.4-mm-thick cylindrical aluminum shell. The combustion tube length was selected to provide a residence time of approximately 60 seconds at a volumetric flow rate of 100 cm³/min in order to completely oxidize the pyrolyzate stream. Published studies of the oxidation of the products of flaming combustion showed that a residence time of 60 seconds at 1000°C was required to completely oxidize the largest size soot particles observed in real fires [27]. However, gaseous pyrolysis products and fire gases are completely (>99%) oxidized in a few seconds at the nominal 900°C combustor temperature, as deduced from high-temperature gas phase oxidation kinetics [28 and 51].
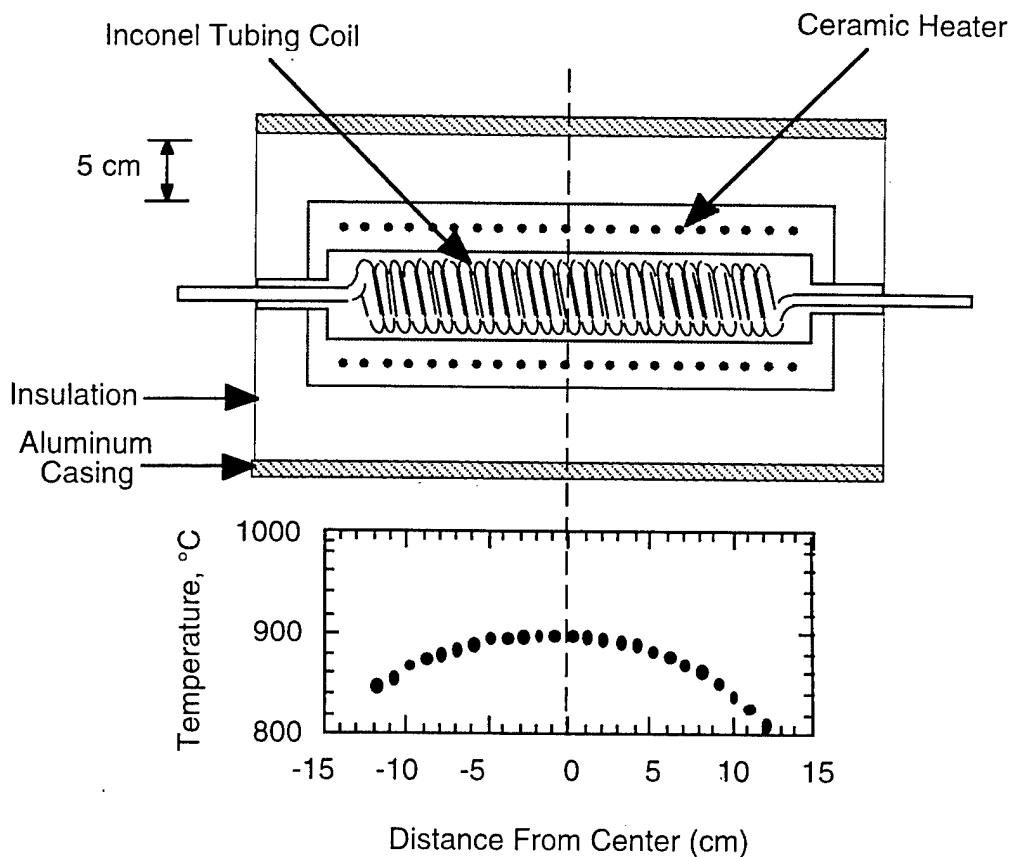

FIGURE 4. COMBUSTOR CROSS SECTION AND TEMPERATURE
DISTRIBUTION FOR 900°C SETPOINT

The temperature distribution along the length of the Inconel tubing coil was measured using a shielded thermocouple probe positioned at several locations along the inside surface of the coil with nitrogen flowing through the coil at 100 cm³/min. These experiments were repeated for various set point temperatures. A nearly symmetric temperature distribution about the coil midpoint location is observed, as shown in figure 4, for the nominal 900°C set point temperature.

COMBUSTION GAS SCRUBBING.

The gas stream exiting the combustor contains nitrogen, combustion products, and unreacted oxygen. This combustion gas stream enters two 6-mm diameter Teflon tubes, 25 cm long, connected in series and tightly packed with anhydrous calcium sulfate (Drierite™) and sodium hydroxide coated silica (Ascarite™), respectively, to remove any H_2O, acid gases, and CO_2 from the sample stream. After cooling and scrubbing, the combustion gas stream contains only nitrogen and the residual oxygen which was not consumed in the combustion reactions. It is important to remove extraneous gases from the combustion stream so that they do not dilute the oxygen measured by the oxygen analyzers. The flow rate of the scrubbed combustion gas stream (≈ 100 cm³/min) is measured by a mass flow meter and continuously recorded by the data acquisition system.

DATA ACQUISITION.

The mass flow rate of pure oxygen entering the nitrogen-pyrolyzate stream is set by the mass flow controller assuming ideal gas behavior. The mass flow rate of oxygen in the scrubbed sample stream after combustion of the volatile polymer degradation products is determined from the measured mass flow rate of the gas stream and the concentration of oxygen measured by a high-speed commercial oxygen analyzer. For the present work, either a polarographic (Rosemount Analytical OM-11 EA) or a zirconia (Panametrics Series 350) oxygen analyzer was used having a 90% response time of less than 1 second and an accuracy ±1% of full scale (0-20% O_2, v/v). Temperatures of the pyrolysis probe, pyrolysis chamber, combustor, and gases are monitored continuously during the test as well as gas and sample stream flow rates and oxygen concentration. Data are acquired at 5 Hz on a personal computer during the experiment using a multichannel data acquisition board and software (National Instruments). To determine the heat release rate from oxygen consumption, the mass flow rate, temperature, and oxygen concentration of the gas stream before and after combustion of the pyrolysis products are measured.

EXPERIMENTAL

MATERIALS.

Polymer samples were unfilled, natural, or virgin-grade resins obtained from Aldrich Chemical Company, Scientific Polymer Products, or directly from manufacturers. Methane, oxygen, and nitrogen gases used for calibration and testing were dry, >99.99% purity grades obtained from Matheson Gas Products, Welco, and Praxair.

INSTRUMENT CALIBRATION.

Steady-state calibrations were performed by metering methane gas directly into the pyrolyzer in a continuous stream and measuring the oxygen depletion of the scrubbed gas stream after complete combustion. Steady-state oxygen depletion was in quantitative agreement with expected values using the net heat of combustion of methane and the stoichiometric fuel/oxygen ratio. Square-wave fuel pulses were generated using a syringe pump containing methane to test the dynamic response of the flow calorimeter to an instantaneously applied ($\beta = \infty$) heat release rate. A characteristic time $\tau = 6$ seconds for the instrument was obtained from the dynamic response of the oxygen depletion

signal to the step change in methane flow (heat release rate) as per equation A-6 in the appendix A. Equation 5 with τ = 6 seconds was then used to deconvolute the oxygen consumption history for the square-wave methane heat release rate pulse with the results shown in figure 5. It is seen that the pulse-shape fidelity of the deconvoluted heat release rate is very good with only a slight overshoot at the step changes because of signal noise.
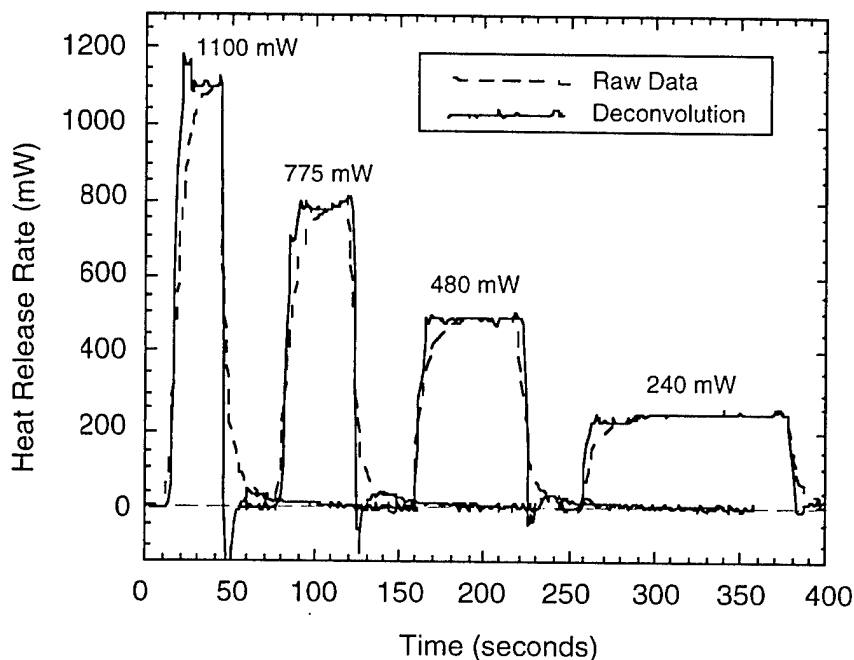

FIGURE 5. HEAT RELEASE RATE SIGNAL FOR SQUARE WAVE METHANE CALIBRATION PULSES BEFORE AND AFTER SIGNAL DECONVOLUTION

TEST PROCEDURE.

In the present method, samples are dried for at least 8 hours at 75°C in a convection oven and held in a dessicant chamber until testing. A dry sample weighing 1.0 ±0.2 milligrams is placed into a preweighed, thin-walled, quartz capillary tube which is 2.5 mm in diameter and 10-12 mm long. The sample and tube are weighed on a microbalance to an accuracy of ±2 micrograms to determine the initial (m_0) and final (m) sample mass after subtracting the weight of the quartz tube. The quartz tube containing the sample is inserted into the heating coil of the pyrolysis probe and the probe is inserted into the pyrolysis chamber and sealed. The pyrolysis chamber is equilibrated at a temperature which is a few degrees below the onset degradation temperature of the sample determined in separate TGA experiments at a heating rate in the range of 10 K/min. A heating rate calibration is performed using a fine thermocouple in a quartz sample tube to measure the actual rate of temperature rise of the sample at the nominal programmed rate.

A constant rate of temperature rise (ramp) is used to heat the sample to a hold (soak) temperature which is well above the thermal decomposition range of typical combustible solids. The ramp and high temperature soak program forces complete thermal decomposition of most combustible solids, so that equations 6 through 8 apply and the heat release rate has physical significance in terms of material properties. Selecting a hold temperature which corresponds to a particular fire environment (heat flux), but which is within the normal temperature range of the polymer thermal decomposition, discriminates between materials with regard to heat resistance but not fire resistance since, in general, the fire heat flux is not known apriori. Therefore, in order to obtain an unambiguous measure of the capacity of a combustible material to release heat in a fire, the standard pyrolysis-

combustion heat release rate test involves heating the sample at a constant rate (260 K/min, typically) to a maximum temperature of 930°C and holding the sample at the maximum temperature for 10 to 120 seconds to effect complete pyrolysis. The volatile pyrolysis products are generated during the temperature ramp and are swept from the pyrolyzer by nitrogen gas flowing at 82 cm³/min to which is added 18 cm³/min of pure oxygen at the inlet to the combustor. Combustion gases are scrubbed to remove carbon dioxide, water, and acid gases (if any), and the gas stream passes through the flow meter and oxygen analyzer. Deconvolution of the oxygen consumption signal is performed during the test, and the heat release rate, heat release capacity, and total heat of combustion are calculated and displayed. The quartz tube is weighed after the test to determine the mass of sample residue.

RESULTS

All data reported in this section are an average of values from 3-5 tests. The repeatability of heat release rate measurements for a single operator is estimated to be ±3% and accuracy is ±7%, with the majority of the error associated with moisture pickup during the weighing and handling of small (1 mg) samples and the noise in the deconvoluted signal. Repeatability and accuracy of total heats of combustion obtained by time integration of the heat release rate is ±5%.

HEAT RELEASE RATE.

Figure 6 shows experimental heat release rate data for several polymers heated at a constant rate of 260 K/min to a maximum temperature of 930°C and held at the maximum temperature for 10 seconds. Included in this data are polyethylene (PE), polypropylene (PP), polystryene (PS), acrylonitrile-buatdiene-styrene terpolymer (ABS), polymethylmethacrylate (PMMA), polyethyleneterphthalate (PET), polyetheretherketone (PEEK), and polybenzimidazole (PBI). It is seen that the maximum specific heat release rates of these commercial polymers varies by more than a factor of 10 and that the magnitude is in qualitative agreement with their flammability as ranked in small scale ignition tests [52].
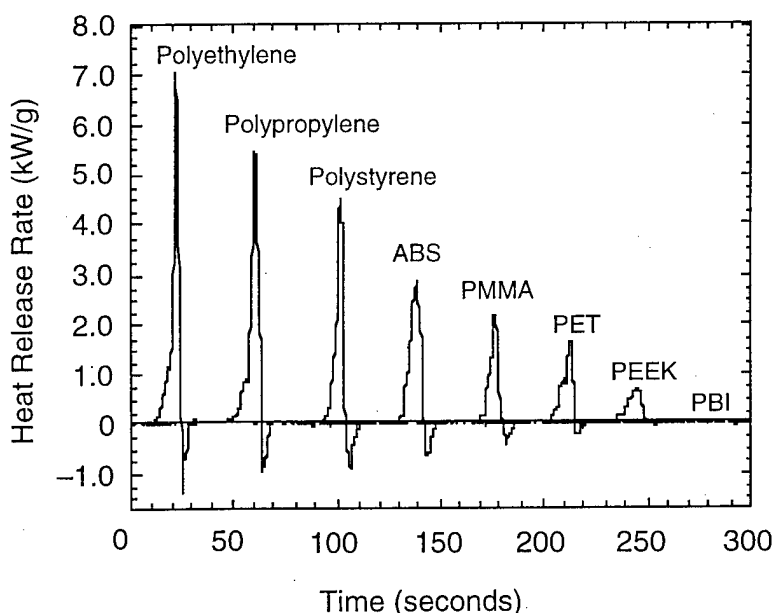

FIGURE 6. SPECIFIC HEAT RELEASE RATE DATA FOR SEVERAL
COMMON POLYMERS AT A HEATING RATE OF 260 K/min
(Horizontally shifted for clarity)

11

Experiments were conducted in which the heat release rate of 1-milligram samples of several common polymers was measured for heating rates ranging from 0.1 to 10 K/s. Figure 7 shows the results of these experiments plotted as the maximum specific heat release rate versus heating rate. Below a heating rate of about 5 K/s, the maximum specific heat release rate is proportional to the sample heating rate as per equation 7 with slope equal to the heat release capacity of the sample as per equation 8. Above a heating rate of about 5 K/s, the specific heat release rate is no longer proportional to the heating rate due to thermal lag of the sample and quartz tube. In practice, a single heating rate below the proportional limit (β = 4.3 K/s, typically) is used for the experiment and the maximum heat release rate is divided by it to obtain the heat release capacity.
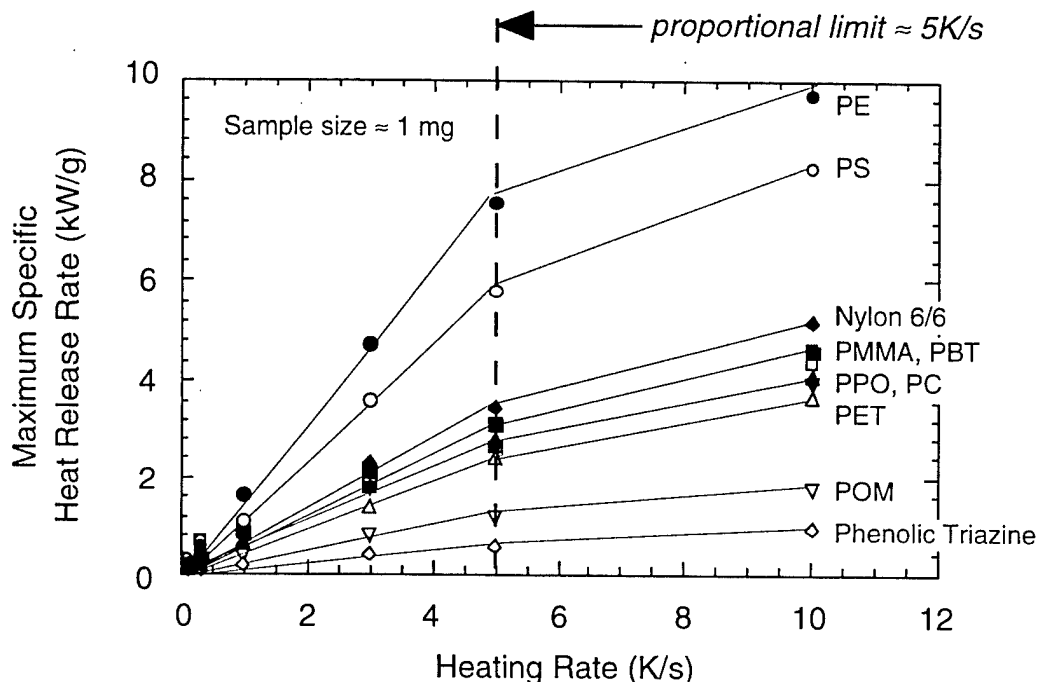

FIGURE 7. SPECIFIC HEAT RELEASE RATE VERSUS HEATING RATE FOR
1-milligram SAMPLES OF SEVERAL COMMON POLYMERS

HEAT RELEASE CAPACITY.

Heat release capacities were calculated by dividing the maximum specific heat release rate of the sample (c.f., figure 7) by the actual heating rate in the test (260 K/min) and the results compared to values obtained from TGA-gas chromatography/mass spectrometry data (TGA/GC-MS) [44 and 53] at a heating rate of 10 K/min. In the TGA/GC-MS, the instantaneous heat of combustion, $h^o_{c,v}(t)$, at peak mass loss rate was computed from the thermochemistry of the major species identified by mass spectroscopy. The heats of combustion so calculated were multiplied by the instantaneous maximum fractional mass loss rate in the TGA to obtain the maximum specific heat release rates as per equation 1. Dividing the maximum heat release rate by the initial sample mass and heating rate β = 10 K/min gives the TGA-GC/MS heat release capacity for comparison to the direct determination by PCFC at β = 260 K/min. Results for the same samples tested by the two different test methods are shown in table 1. The average weighted difference between the heat release capacities obtained by the two different techniques (i.e., PCFC and TGA/GC-MS) is ±9% for the 14 polymers in table 1.

TABLE 1. HEAT RELEASE CAPACITIES MEASURED BY PCFC AND TGA-GC/MS

Polymer	Heat Release Capacity (J/g-K)	
	PCFC (β = 260 K/min)	TGA/GC-MS (β = 10 K/min)
Polyethyene (PE)	1600	1422
Polyproplylene (PP)	1391	1338
Polystyrene (PS)	1198	1302
Poly(α-methyl)styrene	730	695
Polyphenyleneoxide (PPO)	553	635
Polyhexamethyleneadipamide (nylon 6,6)	494	509
Polyethyleneterphthalate (PET)	393	407
Polycarbonate (PC)	390	470
Polymethylmethacrylate (PMMA)	376	360
Poly(p-aramide) (KEVLAR™)	292	207
Polyoxymethylene (POM)	261	233
Polyetheretherketone (PEEK)	180	222
Polyphenylenesulfide (PPS)	156	118
Polyimide (PI)	29	31

HEATS OF COMBUSTION.

Experiments were conducted using dry air as the purge gas in the pyrolyzer during the heating cycle so that the sample was pyrolyzed in the presence of oxygen and all of the char was oxidized during a 2-minute hold period at 930°C. Figure 8 shows heat release rate data for oxidative pyrolysis of the polycarbonate of bisphenol-A (PC)—a polymer which normally shows a single heat release rate peak and forms about 20%-25% char when pyrolyzed under anaerobic conditions. The total oxygen consumed in this experiment is proportional to the net heat of complete combustion of the polymer as determined in an oxygen bomb calorimeter [24 and 54]. The net heat of complete combustion calculated from oxygen consumption and equation 4 as the total area under the heat release rate curve is 29.1 kJ/g, which is in agreement with literature values for this polymer [22 and 54]. Table 2 shows that the net heats of complete combustion measured by PCFC agree with literature values [22 and 54] to within 2% average relative error for the 10 polymers listed in table 2.
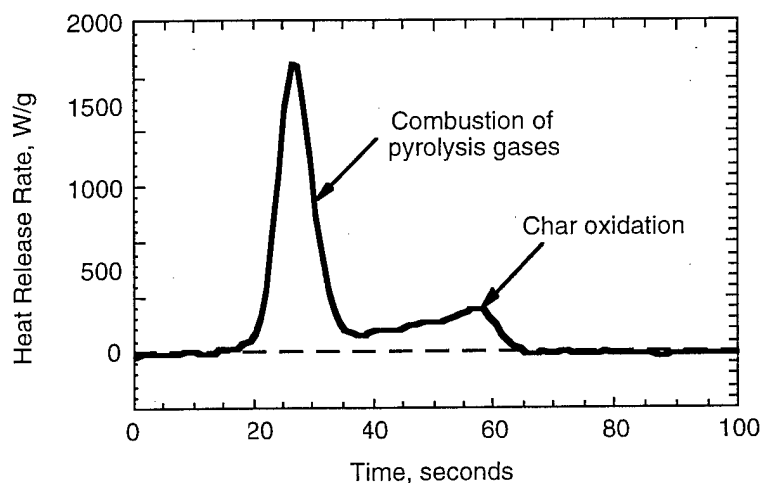

FIGURE 8. HEAT RELEASE RATE FOR OXIDATIVE PYROLYSIS-
COMBUSTION OF POLYCARBONATE

13

TABLE 2. NET HEATS OF COMBUSTION (kJ/g) OF SELECTED POLYMERS BY
PCFC AND OXYGEN BOMB CALORIMETRY

Polymer	PCFC	Oxygen Bomb
Polyethylene	44.1	43.3
Polystyrene	40.1	39.8
Polyetheretherketone	30.9	30.2
Phenolic Triazine	29.5	29.8
Polycarbonate	29.1	29.8
Poly(p-aramide)	28.1	27.8
Polybutyleneterephthalate	26.3	26.7
Polymethylmethacrylate	25.0	24.9
Polyethyleneterephthalate	23.2	21.8
Polyoxymethlene	15.0	15.9

DISCUSSION

Pyrolysis-combustion flow calorimetry is a verified method for measuring static (heat release capacity and total heat) and dynamic (heat release rate) combustion parameters of materials. Early work in our laboratory suggested a proportionality between specific heat release rate and the heat release rate in flaming combustion [55], and recent work [14, 47, and 48] has focused on developing the physical basis for this relationship and improving the measurement technique. The derived relationship between the average flaming heat release rate HRR (W/m^2) of thick samples measured in a fire calorimeter and the specific heat release rate (W/kg) is [47 and 48]

$$HRR = \chi \rho \delta \, \dot{q}_c^{max} \qquad (9)$$

where χ, ρ, and δ are the combustion efficiency in the flame, polymer density, and the pyrolysis zone depth at the burning surface, respectively, and $\dot{q}_c^{max}$ is the maximum specific heat release rate measured (e.g., by PCFC) at heating rate $\beta = \dot{q}_{net}^2/\kappa\rho h_g$ [47 and 48], where $\dot{q}_{net}$ is the net heat flux into the sample. At an external heat flux typical of large fires and fire calorimeter tests, $\dot{q}_{ext} \approx 50$ kW/m^2, the pyrolysis zone depth is on the order of $\delta = 0.5$ mm [48 and 56], so that for typical $\chi = 0.8 \pm 0.2$, polymer thermal conductivity $\kappa = 0.2$ W/m-K and $\rho = 1100$ kg/m^3, the ratio of the flaming and nonflaming (specific) heat release rates is

$$\frac{HRR}{\dot{q}_c^{max}} = \chi\rho\delta \approx 0.4 \pm 0.2 \, kg/m^2 \qquad (10)$$

The proportionality between the average heat release rate in flaming combustion and the specific heat release rate is confirmed in figure 9 with slope, $HRR/\dot{q}_c^{max} = 0.5$ kg/m^2 in the expected range. The flaming heat release rates plotted in figure 9 are average values over the duration of flaming, taken from the literature [57, 58, 59, 60, and 61] or measured in our laboratory [62 and 63] according to a standard method [20] using 10 x 10 x 0.64 cm (≈ 80 g) polymer samples in a fire calorimeter at an external heat flux $\dot{q}_{ext} = 50$ kW/m^2 (net heat flux, $\dot{q}_{net} \approx 35$ kW/m^2). Specific heat release rates plotted in figure 9 were calculated by multiplying the polymer heat release capacities by the heating rate in the fire calorimeter, $\beta = \dot{q}_{net}^2/\kappa\rho h_g = 2$ K/s.
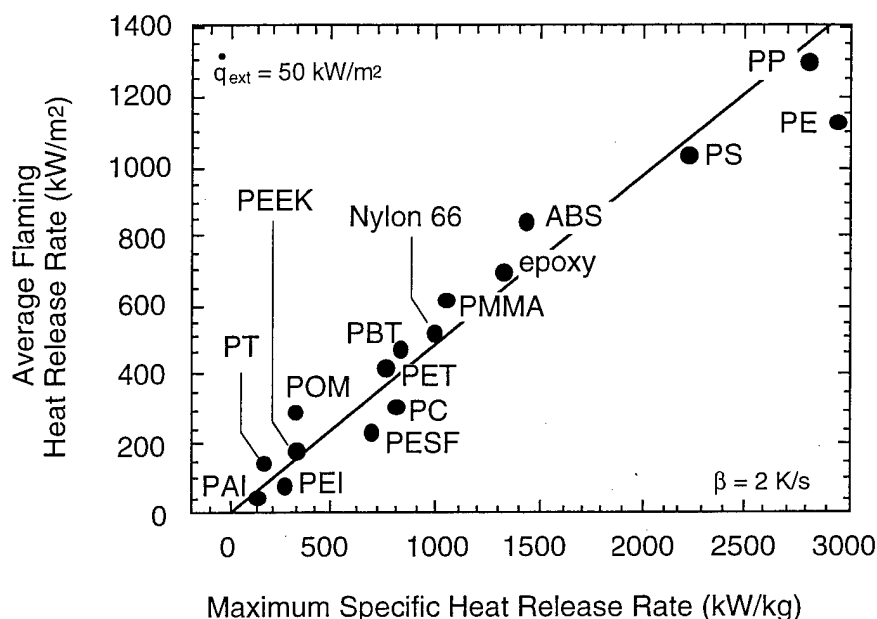
14

FIGURE 9. FLAMING HEAT RELEASE RATE VERSUS NONFLAMING (SPECIFIC) HEAT RELEASE RATE

CONCLUSIONS

Pyrolysis-combustion flow calorimetry (PCFC) is a reproducible, calibrated technique for measuring dynamic and static combustion parameters of materials that provides a convenient methodology for estimating the fire hazard potential of a material using only milligram samples.

REFERENCES

1. V. Babrauskas and R.D. Peacock, "Heat Release Rate: The Single Most Important Variable in Fire Hazard," *Fire Safety Journal*, 18, pp. 255-272, 1992.

2. C.P. Sarkos and R.G. Hill, "Evaluation of Aircraft Interior Panels Under Full Scale Cabin Fire Conditions," Proceedings of the AIAA 23rd Aerospace Sciences Meeting, Reno, NV, January 14-17, 1985.

3. J.G. Quintiere, V. Babrauskas, L. Cooper, M. Harkelroad, K. Steckler, and A. Tewarson, "The Role of Aircraft Panel Materials in Cabin Fires and Their Properties," DOT/FAA/CT-84/30, June 1985.

4. V. Babrauskas, "From Bunsen Burner to Heat Release Rate Calorimeter," in *Heat Release in Fires*, V. Babrauskas and S. Grayson, eds., Elsevier Applied Science, New York, pp. 7-29, 1992.

5. M. Janssens, "Calorimetry," in *SFPE Handbook of Fire Protection Engineering*, 2nd Edition, Chapter 3.2, Society of Fire Protection Engineers, Boston, MA, 1995.

6.   M.J. Scudamore, P.J. Briggs, and F.H. Prager, "Cone Calorimetry–A Review of Tests Carried out on Plastics for the Association of Plastic Manufacturers in Europe," *Fire and Materials*, 15, pp. 65-84, 1991.

7.   V. Babrauskas, "Comparative Rates of Heat Release from Five Different Types of Test Apparatuses," *Journal of Fire Sciences*, 4(2), pp. 148-158, 1986.

8.   T. Kashiwagi and T.G. Cleary, "Effects of Sample Mounting on Flammability Properties of Intumescent Polymers," *Fire Safety Journal*, 20, 203-225, 1993.

9.   A. Tewarson, "Generation of Heat and Chemical Compounds in Fires," in *SFPE Handbook of Fire Protection Engineering*, 2nd Edition, Chapter 3-4, Society of Fire Protection Engineers, Boston, MA, 1995.

10.   E.M. Pearce, Y.P. Khanna, and D. Raucher, "Thermal Anlaysis of Polymer Flammability," in *Thermal Characterization of Polymeric Materials*, E.A. Turi, ed., Academic Press, Orlando, FL, pp. 793-843, 1981.

11.   H.L. Hassel, "Evaluation of Polymer Flammability by Thermal Analysis," *American Laboratory*, January 1977.

12.   T.D. Gracik and G.L. Long, "Prediction of Thermoplastic Flammability by Thermogravimetry," *Thermochimica Acta*, 212, pp. 163-170, 1992.

13.   D.W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, pp. 627-653, 1990.

14.   R.E. Lyon, "Heat Release Capacity," presented at the Fire & Materials Conference, San Francisco, CA, January 22-24, 2001.

15.   R.A. Susott, F. Shafizadeh, and T.W. Aanerud, "A Quantitative Thermal Analysis Technique for Combustible Gas Detection," *Journal of Fire and Flammability*, 10, pp. 94-104, 1979.

16.   R.A. Susott, "Thermal Behavior of Conifer Needle Extractives," *Forest Sciences*, 26(3), pp.147-160, 1980.

17.   R.A. Susott, "Characterization of the Thermal Properties of Forest Fuels by Combustible Gas Analysis," *Forest Sciences*, 28(2), pp. 404-420, 1982.

18.   M. L. Janssens, "Measuring Heat Release by Oxygen Consumption," *Fire Technology*, 27, pp. 234, 1991.

19.   M. Janssens and W.J. Parker, "Oxygen Consumption Calorimetry," in *Heat Release in Fires*, V. Babrauskas and S.J. Grayson, eds., Chapter 3, Elsevier Applied Science, New York, pp. 31-59, 1992.

20.   Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter, ASTM E 1354-90, ASTM Fire Test Standards, 3rd Edition, American Society for Testing of Materials, Philadelphia, PA, pp. 803-817, 1990.

21. C. Huggett, "Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements," *Fire and Materials,* 4(2), p. 61, 1980.

22. V. Babrauskas, "Heat of Combustion and Potential Heat," in *Heat Release in Fires,* V. Babrauskas and S.J. Grayson, eds., Chapter 8, Elsevier Applied Science, New York, pp. 207-232, 1992.

23. W.M. Thornton, *Philosophical. Magazine,* 33, p. 196, 1917.

24. Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter, ASTM D 2015-85, ASTM Fire Test Standards, 3rd Edition, American Society for Testing of Materials, Philadelphia, PA, pp. 222-229, 1990.

25. W.J. Parker, "Prediction of the Heat Release Rate of Wood," Ph.D. Thesis, The George Washington University, April 1988.

26. W.J. Parker, "Determination of the Input Data for a Model of the Heat Release Rate of Wood," in *Mathematical Modeling of Fires,* ASTM STP 983, J.R. Mchaffey, ed., American Society for Testing and Materials, Philadelphia, PA, pp. 105-115, 1987.

27. V. Babrauskas, W.J. Parker, G. Mulholland, and H. Twilley, "The Phi Meter: A Simple, Fuel-Independent Instrument for Monitoring Combustion Equivalence Ratio," *The Review of Scientific Instruments,* 65(7), pp. 2367-2375, 1994.

28. S.M. Reshetnikov and I.S. Reshetnikov, *Polymer Degradation and Stability,* 64, pp. 379-385, 1999.

29. S.M. Reshetnikov and GA Prevozchikov, USSR 285663, January 2, 1998.

30. D. Price, F.Gao, G.J. Milnes, B. Eling, C.I. Lindsay, and P.T. McGrail, "Laser Pyrolysis/Time-of-Flight Mass Spectrometry Studies Pertinent to the Behavior of Flame Retarded Polymers in Real Fire Situations," *Polymer Degradation and Stability,* 64, pp. 403-410, 1999.

31. S.M. Angel, "In Situ Flame Chemistry by Remote Spectroscopy," in *Fire Resistant Materials: Progress Report,* R.E. Lyon, ed., DOT/FAA/AR-97/100, p. 229, November 1998.

32. W.W. Wendlandt in *Thermal Methods of Analysis,* 2nd Edition, John Wiley & Sons, New York, Chapter V.C., 1974.

33. R.E. Lyon, "An Integral Method of Nonisothermal Kinetic Analysis," *Thermochimica Acta,* 297, pp.117-124, 1997.

34. B. Wunderlich, in *Thermal Characterization of Polymeric Materials,* E.A. Turi, ed., Academic Press, Inc., New York, NY, Chapter 2.D, p. 112, 1981.

35. Flynn and L.A. Wall, "General Treatment of the Thermogravimetry of Polymers," *Journal of Research of the National Bureau of Standards–A Physics and Chemistry,* 70A (6), p. 487, 1966.

36.   R.E. Lyon, "Pyrolysis Kinetics of Char Forming Polymers," *Polymer Degradation and Stability*, 61(2), pp. 201-210, 1998.

37.   T.D. Gracik and G.L. Long, "Heat Release and Flammability of a Small Specimen Using Thermoanalytical Techniques," in *Fire Calorimetry,* proceedings from the 50th Calorimetry Conference, R.E. Lyon and M.M. Hirschler eds., Gaithersburg, MD, DOT/FAA/CT-95/46, p. 101, 1995.

38.   T.D. Gracik, G.L. Long, U.A.K. Sorathia, and H.E. Douglas, "A Novel Thermogravimetric Technique for Determining Flammability Characteristics of Polymeric Materials," *Thermochimica Acta*, pp. 212, 209-217, 1992.

39.   A. Tewarson and R.F. Pion, "Flammability of Plastics-I. Burning Intensity," *Combustion and Flame*, 26, pp. 85-103, 1976.

40.   A. Tewarson, "Experimental Evaluation of Flammability Parameters of Polymeric Materials," in *Flame Retardant Polymeric Materials*, M. Lewin, S.M. Atlas, and E.M. Pearch, eds., Ch. 3, pp. 97-153, Plenum Press, New York, 1982.

41.   E.W. Kifer and L.H. Leiner, "Thermal Evolution Analysis of Some Organic Materials," *Analytical Calorimetry*, Plenum Press, NY, pp. 199-205, 1974.

42.   R.N. Walters and R.E. Lyon, "A Microscale Combustion Calorimeter for Determining Flammability Parameters of Materials," presented at NIST Annual Conference on Fire Research, Gaithersburg, MD, October 30, 1996.

43.   R.N. Walters and R.E. Lyon, "A Microscale Heat Release Rate Device," presented at Society of Plastics Engineers Annual Technical Conference (ANTEC 96), Indianapolis, IA, May 5-9, 1996.

44.   T.V. Inguilizian, "Correlating Polymer Flammability Using Measured Pyrolysis Kinetics," Masters Thesis, University of Massachusetts (Amherst), January 1999.

45.   N. Grassie, "Products of Thermal Degradation of Polymers," in *Polymer Handbook*, Third Edition, J. Brandrup and E.H. Immergut, eds., Third Edition, Chapter II, John Wiley & Sons, NY, pp. 365-386, 1989.

46.   CF Cullis, MM Hirschler, *The Combustion of Organic Polymers*, Oxford, England: Claredon Press, 1981.

47.   R.E. Lyon, "Solid-State Thermochemistry of Flaming Combustion," in *Fire Retardancy of Polymeric Materials*, A.F. Grand and C.A. Wilkie, eds., Marcel Dekker, NY, 2000, pp. 391-447.

48.   R.E. Lyon, "Heat Release Kinetics," *Fire and Materials*, 24, pp. 179-186, 2000.

49.   Standard Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High Precision Method), ASTM-D238, American Society for Testing of Materials, Philadelphia, PA, 1988.

50. T.B. Brill, P.J. Brush, K.J. James, J.E. Shepherd, and K.J. Pfeiffer, "T-Jump/FT-IR Spectroscopy: A New Entry into the Rapid, Isothermal Pyrolysis Chemistry of Solids and Liquids," *Applied Spectroscopy*, 46(6), pp. 900-911, 1992.

51. W.M. Heffington, G.E. Parks, K.G.P. Sulzmann, and S.S. Penner, "Studies of Methane Oxidation Kinetics," Proceedings of the Sixteenth Symposium (International) on Combustion, the Combustion Institute, pp. 997-1010, 1976.

52. Plastics Digest, Edition 17, Volume 1, "Themoplastics and Thermosets: Flammability Data," D.A.T.A. Business Publishing, Englewood, CO, pp. 773-889, 1996.

53. H.Q. Zhang, P.R. Westmoreland, and R.J. Farris, "Understanding the Fire Behavior of Polymers," presented at the Cooperative University of Massachusetts-Industry Research on Polymers Meeting (Fire Safe Polymers and Polymer Composites Cluster), May 11, 2000, Amherst, MA.

54. R.N. Walters, S.M. Hackett, and R.E. Lyon, "Heats of Combustion of High-Temperature Polymers," *Fire and Materials*, 24(5), pp. 245-252, 2000.

55. R.E. Lyon, "Material Properties and Heat Release Rate of Polymers," presented at the 50th Calorimetery Conference, Gaithersburg, MD, July 23-28, 1995.

56. H.E. Thomson and D.D. Drysdale, "Flammability of Plastics," *Fire and Materials*, 11, pp. 163-172, 1987.

57. M.J. Scudamore, P.J. Briggs, and F.H. Prager, "Cone Calorimetry–A Review of Tests Carried out on Plastics for the Association of Plastic Manufacturers in Europe," *Fire and Materials*, 15, pp. 65-84, 1991.

58. V. Babrauskas, "Comparative Rates of Heat Release from Five Different Types of Test Apparatuses," *Journal of Fire Sciences*, 4(2), pp. 148-158, 1986.

59. T. Kashiwagi and T.G. Cleary, "Effects of Sample Mounting on Flammability Properties of Intumescent Polymers," *Fire Safety Journal*, 20, pp. 203-225, 1993.

60. M.M. Hirschler, "Heat Release from Plastic Materials," in *Heat Release in Fires*, V. Babrauskas and S. Grayson, eds., Elsevier Applied Science, New York, pp. 375-422. 1992.

61. P.K. Kim, P. Pierini, and R. Wessling, "Thermal and Flammability Properties of Poly(p-phenylenebenzobisoxazole), in Proc. 39th Sagamore Conference on The Science and Technology of Fire Resistant Materials, D.P. Macaione, ed., p. 327-338, 1992.

62. R.E. Lyon, S. Gandhi, and R.N. Walters, "Flammability Study of Advanced Engineering Thermoplastics," presented at the Society for the Advancement of Materials and Process Engineering (SAMPE) 44th International Symposium and Exhibition, Long Beach, CA, May 23-27, 1999.

63. S. Gandhi, R.N. Walters, and R.E. Lyon, "Cone Calorimeter Study of Cyanate Esters for Aircraft Applications," presented at the 27th International Conference on Fire Safety, San Francisco International Airport, CA, January 11-15, 1999.

APPENDIX A—FLOW MODEL FOR DECONVOLUTION

In the pyrolysis-combustion flow calorimeter (figure 1), the oxygen concentration is measured several meters downstream from the point at which the pyrolysis gases are generated, mixed with excess oxygen in the heated manifold, and enter the combustor. As the oxygen depletion profile moves through the 6-mm (1/4-inch) diameter tubing of the instrument, mixing and diffusion of the flow stream in the combustor and scrubbers tends to broaden and attenuate the peak. These effects must be corrected to synchronize the fuel generation history of the sample with the oxygen consumption history measured at the downstream detector.

The oxygen signal distortion is assumed to be the result of simple mixing in a perfectly stirred dead volume, V_0, which may be distributed over the flow path. In this case, the mass of oxygen in the mixing volume at any time is

$$m_{O_2} = \rho V_0 [O_2] = \rho V_0 [O_2]^{out} \tag{A-1}$$

where ρ is the gas density and $[O_2]$ is the instantaneous volume fraction (concentration) of oxygen in the gas stream which, if V_0 is well mixed, is equal to the oxygen concentration leaving V_0 and entering the detector, so $[O_2] = [O_2]^{out}$. For a constant volumetric flow F, the change in the mass of oxygen in the mixing volume over any time interval, dt, is

$$d\, m_{O_2} = \left(\dot{m}_{O_2}^{in} - \dot{m}_{O_2}^{out} \right) dt = \left(\rho F \left[O_2 \right]^{in} - \rho F \left[O_2 \right]^{out} \right) dt \tag{A-2}$$

where $\dot{m}_{O_2}^{in}$ and $\dot{m}_{O_2}^{out}$ are the mass flow rates of oxygen into and out of the well mixed volume, V_0, Differentiating equation A-1 with respect to time and equating the result to the differential form of equation A-2

$$\Delta \dot{m}_{O_2} \equiv \dot{m}_{O_2}^0 - \dot{m}_{O_2}^{in} = \rho F \left[O_2 \right]^0 - \rho F \left[O_2 \right]^{in} = \rho F \left(\left[O_2 \right]^0 - \left[O_2 \right]^{out} \right) - \rho V_0 \frac{d \left[O_2 \right]^{out}}{dt} \tag{A-3}$$

where $\dot{m}_{O_2}^0$ is the base line mass flow rate of oxygen and $\Delta \dot{m}_{O_2}$ is the mass consumption rate of oxygen relative to the base line. Making the substitutions, $\theta = [O_2]^0 - [O_2]^{out}$ and $\tau = V_0/F$, the specific heat release rate in terms of the oxygen concentration at the detector is

$$\dot{Q}_c(t) \equiv E\, \Delta \dot{m}_{O_2}(t) = C \left(\theta + \tau \frac{d\theta}{dt} \right) \tag{A-4}$$

A-1

where $C = E\rho F$ (a constant with units of Watts). Equation A-4 synchronizes the oxygen signal with the heat release history of the solid. Inverting equation A-4

$$\theta(t) = \frac{1}{C\tau} \int_{-\infty}^{t} \exp\left(-(t-\xi)/\tau\right) \dot{Q}_c(\xi)\, d\xi \tag{A-5}$$

shows that the oxygen depletion measured at the detector $\theta(t)$ is distorted (convoluted) by an exponential apparatus function. The convolution integral (equation A-5) can be solved exactly for a heat release rate history that has an analytic form. An experimentally convenient heating history is a step change in heat release rate, i.e., $\dot{Q}_c(t) = 0$ for $-\infty < t < 0$, and, $\dot{Q}_c(t) = \dot{Q}_c^0$ (a constant) for $t \geq 0$, which when substituted into equation A-5 and solved

$$\theta(t) = \frac{\dot{Q}_c^0}{C\tau} \int_{-\infty}^{t} \exp\left(-(t-\xi)/\tau\right) u(\xi)\, d\xi = \frac{\dot{Q}_c^0}{C}\left(1 - \exp\left(-(t/\tau)\right)\right) \tag{A-6}$$

shows that θ approaches an equilibrium value $\dot{Q}_c^0/C$ as $t \to \infty$, and that, $t = \tau$ when θ equals 63% of this steady-state value for a constant heat flow $\dot{Q}_c^0$. This result and the step change heating history is the basis of the calibration procedure for the PCFC (see figure 5).